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(54) **METHODS FOR INCREASING THE EXTRACTABLE RUBBER CONTENT OF NON-HEVEA PLANT MATTER**

(57) Methods for increasing the extractable rubber content of non-*Hevea* plant matter that entail the use of particular forms of hammer milling and/or roller milling in an increase in the amount of rubber that can be extracted from the resulting plant matter such as by organic solvent extraction or aqueous extraction are provided. In certain embodiments, the methods are for increasing the extract-

able rubber content of guayule plant matter, and entail the use of particular forms of hammer milling in combination with roller milling and flaking to increase the amount of rubber that can be extracted from the guayule plant matter such as by organic solvent extraction or aqueous extraction.

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DescriptionBACKGROUND

5 **[0001]** The *Hevea* plant or tree (also called *Hevea brasiliensis* or a rubber tree) is a well-known source of natural rubber (also called polyisoprene). Rubber sources such as *Hevea brasiliensis*, *Ficus elastica* (India rubber tree) and *Cryptostegia grandiflora* (Madagascar rubbervine) produce natural rubber in the form of a sap where the rubber is suspended in an aqueous solution that flows freely and can be recovered by tapping of the plant. Various non-*Hevea* plants are also known to contain natural rubber, but their rubber is stored within the individual cells of the plant (e.g., stems, roots or leaves) and cannot be accessed by tapping but can only be accessed by breaking down the cell walls by physical or other means.

SUMMARY

15 **[0002]** Provided herein are methods for increasing the extractable rubber content of non-*Hevea* plant matter. The methods comprise the use of particular forms of hammer milling and/or roller milling and result in an increase in the amount of rubber that can be extracted from the resulting plant matter such as by organic solvent extraction or aqueous extraction.

20 **[0003]** In a first embodiment, a method for increasing the extractable rubber content of non-*Hevea* plant matter without unduly increasing the extractable resin content is provided. The method comprises utilizing a quantity of chopped non-*Hevea* plant matter having an average length of ½" to 4" and a maximum moisture content of about 15 weight % and subjecting the chopped non-*Hevea* plant matter to at least one of hammer milling utilizing a screen size of less than ½" and roller milling with corrugated rolls having no more than 12 grooves per inch, thereby producing a quantity of milled non-*Hevea* plant matter. The milled non-*Hevea* plant matter has a maximum moisture content of about 15 weight %, an extractable rubber content at least 30% higher than the pre-milled chopped non-*Hevea* plant matter.

25 **[0004]** In a second embodiment, a method for increasing the extractable rubber content of guayule shrub plant matter without unduly increasing the extractable resin content is provided. The method comprises utilizing a quantity of chopped guayule shrub having an average length of ½" to 4" and a maximum moisture content of about 15 weight % and subjecting the chopped guayule shrub plant matter to hammer milling utilizing a screen size of less than ½"; optionally roller milling with corrugated rolls having no more than 12 grooves per inch, and flake milling, thereby producing a quantity of milled guayule shrub plant matter. The milled guayule shrub plant matter has a maximum moisture content of about 15 weight %, an extractable rubber content at least 100% higher than the pre-milled chopped guayule shrub plant matter and an extractable resin content no more than 3 times the extractable rubber content.

35 DETAILED DESCRIPTION

[0005] The methods provided herein relate to increasing the extractable rubber content of non-*Hevea* plant matter. The methods comprise the use of particular forms of hammer milling and/or roller milling and result in an increase in the amount of rubber that can be extracted from the resulting plant matter such as by organic solvent extraction or aqueous extraction.

Definitions

45 **[0006]** The terminology as set forth herein is for description of the embodiments only and should not be construed as limiting the invention as a whole.

[0007] As used herein, the term non-*Hevea* plant is intended to encompass plants that contain natural rubber within the individual cells of the plant.

[0008] As used herein the term "plant matter" means material obtained from a non-*Hevea* plant. Unless otherwise specified, the plant matter may include roots, stems, bark, woody material, pith, leaves and dirt.

50 **[0009]** As used herein the term "resin" means the naturally occurring non-rubber chemical entities present in non-*Hevea* plant matter, including but not limited to resins (such as terpenes), fatty acids, proteins, and inorganic materials.

The Methods

55 **[0010]** In a first embodiment, a method for increasing the extractable rubber content of non-*Hevea* plant matter without unduly increasing the extractable resin content is provided. The method comprises utilizing a quantity of chopped non-*Hevea* plant matter having an average length of ½" to 4" and a maximum moisture content of about 15 weight % and subjecting the chopped non-*Hevea* plant matter to at least one of hammer milling utilizing a screen size of less than

½" and roller milling with corrugated rolls having no more than 12 grooves per inch, thereby producing a quantity of milled non-*Hevea* plant matter. The milled non-*a* maximum moisture content of about 15 weight %, an extractable rubber content at least 30% higher than the pre-milled chopped non-*Hevea* plant matter and an extractable resin content of no more than 3 times the extractable rubber content.

[0011] In certain sub-embodiments according to the first embodiment, the non-*Hevea* plant matter is from guayule shrubs. Thus, disclosed and discussions contained herein that are directed to the first embodiment should be understood to apply equally to this sub-embodiment of the first embodiment, unless indicated otherwise.

[0012] In a second embodiment, a method for increasing the extractable rubber content of guayule shrub plant matter without unduly increasing the extractable resin content is provided. The method comprises utilizing a quantity of chopped guayule shrub having an average length of ½" to 4" and a maximum moisture content of about 15 weight % and subjecting the chopped guayule shrub plant matter to hammer milling utilizing a screen size of less than ½"; optionally roller milling with corrugated rolls having no more than 12 grooves per inch, and flake milling, thereby producing a quantity of milled guayule shrub plant matter. The milled guayule shrub plant matter has a maximum moisture content of about 15 weight %, an extractable rubber content at least 100% higher than the pre-milled chopped guayule shrub plant matter and an extractable resin content no more than 3 times the extractable rubber content.

[0013] As previously mentioned, the methods according to the first embodiment disclosed herein are utilized with plant matter from non-*Hevea* plants. Exemplary non-*Hevea* plants useful in those methods, include, but are not limited to: *Parthenium argentatum* (Guayule shrub), *Taraxacum Kok-Saghyz* (Russian dandelion), *Euphorbia lathyris* (gopher plant), *Parthenium incanum* (mariola), *Chrysothamnus nauseosus* (rabbitbrush), *Pedilanthus macrocarpus* (candillilla), *Asclepias syriaca*, *speciosa*, *subulata*, et al (milkweeds), *Solidago altissima*, *graminifolia rigida*, et al (goldenrods), *Cacalia atriplicifolia* (pale Indian plantain), *Pycnanthemum incanum* (mountain mint), *Teucreum canadense* (American germander) and *Campanula Americana* (tall bellflower). Other plants which produce rubber and rubber-like hydrocarbons are known, particularly among the Compositae, Euphorbiaceae, Campanulaceae, Labiatae, and Moracea families. The plant matter that is processed according to the first and second embodiments of the methods disclosed herein, can be from one type of plant or a mixtures of more than one type of plant.

[0014] As previously discussed, in the first embodiments of the methods disclosed herein, the extractable rubber content of the milled plant material is at least 30% higher and in the second embodiment at least 100% higher than the extractable rubber content of the pre-milled chopped plant matter. In certain embodiments according to the first embodiments of the methods disclosed herein, the extractable rubber content of the milled plant material is at least 40% higher, at least 50% higher or even at least 60% higher than the extractable rubber content of the pre-milled chopped plant matter. In certain embodiments of the first embodiment of the methods disclosed herein, the extractable rubber content of the milled plant material is at least 30% higher and the extractable resin content is no more than 3 times, no more than 2 times or no more than 1.5 times higher than in extractable contents in the pre-milled chopped plant matter. In certain embodiments of the second embodiments disclosed herein, the extractable rubber content of the milled plant material is at least 100% higher and the extractable resin content is no more than 3 times, no more than 2 times, or no more than 1.5 times higher than the extractable contents of the pre-milled chopped plant matter. In certain embodiments according to the first embodiments of the methods disclosed herein, the extractable rubber content of the milled plant material is at least 40% higher, at least 50% higher or even at least 60% higher than the extractable rubber content of the pre-milled chopped plant matter. Exemplary methods for measuring the extractable rubber content and the extractable resin content of milled plant material are provided in the Examples.

[0015] In certain embodiments according to the first and second embodiments of the methods disclosed herein, the milled plant matter has an extractable resin content of no more than 3 times the extractable rubber content. In certain other embodiments according to the first and second embodiments of the method disclosed herein, the milled plant matter has an extractable resin content of no more than 2 times the extractable rubber content. In yet other embodiments according to the second embodiment of the methods disclosed herein, the milled plant matter has an extractable resin content of no more than 1.5 times the extractable rubber content. As illustrated in the Examples provided, herein, it is believed that the use of flake milling in combination with hammer milling and roller milling allows for an increase in extractable rubber content without an unduly commensurate increase in extractable resin content (as compared to hammer milling and roller milling alone). As used herein, the phrase without unduly increasing the extractable resin content is used to refer to an increase in extractable rubber content of a given plant material that is higher than the commensurate increase in extractable resin content of that plant material (e.g., extractable rubber content increases by 50%, but extractable resin content only increases by 20%), each as compared to extractable contents on pre-milled chopped plant material. In certain embodiments according to the first and second embodiments disclosed herein, the methods can be understood as resulting in a preferential (or larger) increase in extractable rubber content as compared to any increase in extractable resin content. In certain instances, it may be preferable to increase the extractable rubber content without unduly increasing the extractable resin content.

[0016] In certain embodiments according to the first embodiment of the methods disclosed herein, the non-*Hevea* plant matter is obtained from at least one of: *Parthenium argentatum* (Guayule shrub), *Taraxacum Kok-Saghyz* (Russian

dandelion), *Euphorbia lathyris* (gopher plant), *Parthenium incanum* (mariola), *Chrysothamnus nauseosus* (rabbitbrush), *Pedilanthus macrocarpus* (candililla), *Asclepias syriaca*, *speciosa*, *subulata*, et al (milkweeds), *Solidago altissima*, *graminifolia rigida*, et al (goldenrods), *Cacalia atriplicifolia* (pale Indian plantain), *Pycnanthemum incanum* (mountain mint), *Teucreum canadense* (American germander) and *Campanula Americana* (tall bellflower). In certain preferred embodiments according to the first and second embodiments of the methods disclosed herein, the non-*Hevea* plant matter is obtained from guayule shrub (*Parthenium argentatum*).

[0017] According to the first and second embodiments of the methods disclosed herein, the plant matter that is utilized has been chopped. In certain embodiments, the plant matter comprises chopped guayule shrub including bark and woody tissue from the shrub but with no more than 5 weight %, preferably no more than 4 weight % or no more than 3 weight % or even more preferably no more than 1 weight % of the plant matter comprising leaves from the guayule shrub. In certain of the foregoing embodiments, the chopped guayule shrub used initially comprises both the above-ground portions and below-ground portions of the shrub (i.e., the stems (with bark, woody tissue and pith) and the roots). In other of the foregoing embodiments, the guayule shrub used comprises only the above-ground portions of the shrub (in other words, the roots are not included in the plant matter). The leaves of the guayule shrub may be removed using various methods such as field drying followed by shaking. Other methods for removing the leaves from the guayule shrub may be utilized as the particular method for removing leaves is not considered to be a significant limitation of the processes disclosed herein. In certain embodiments where the plant matter comprises guayule shrub, the shrubs are harvested by removing the entire plant (with roots intact) and allowing it to dry in the field to a water content of no more than 15 weight %, preferably no more than 12 weight % or even no more than 10 weight % water.

[0018] As previously discussed, the chopped plant matter or chopped guayule shrub plant matter that is processed according to the methods of the first and second embodiments disclosed herein has a maximum moisture content of no more than about 15 weight % (based on the total weight of the chopped plant matter). As used herein, the term no more than about 15 weight % moisture should be understood to include moisture contents of 20 weight % and less, 15 weight % and less, including 5-20 weight % moisture, 5-15 weight % moisture, 10-15 weight % moisture and 10-20 weight % moisture. In other embodiments according to the first and second embodiments disclosed herein, the chopped plant matter or chopped guayule shrub plant matter has a maximum moisture content of 12 weight % or even a maximum moisture content of 10 weight %. The moisture content includes the water content in addition to any organic solvents that may be added to the chopped plant matter or chopped guayule plant matter. Preferably, the chopped plant matter or chopped guayule shrub plant matter that is processed according to the methods of the first and second embodiments disclosed herein contains no added organic solvent and, thus, its "moisture content" is the result of residual water present from the harvested plant matter or guayule shrub material.

[0019] In certain embodiments of the first and second embodiments of the methods disclosed herein, the plant matter utilized in the slurry has been chipped or chopped into pieces with an average size of 1" or less. (Unless indicated to the contrary, the terms chipping and chopping, and various forms of each, are used interchangeably herein.) The chipping or chopping may take place in one or more than one step. For example, the non-*Hevea* plant that is utilized may be rough chopped at the location of harvesting into pieces averaging less than 2" in length. Alternatively, the non-*Hevea* plant that is utilized may be rough chopped into pieces of about 3" in length. Rough chopping may take place before or after the optional removal of leaves and soil (such as by shaking the plant or subjecting it to strong air currents), but is preferably after the removal of a large majority of leaves and soil from the harvested plant matter. Chipping or chopping into pieces with an average size of 1.5" or less or 1" or less may be achieved using various physical means. One exemplary way of obtaining chopped plant matter with an average size of 1.5" or less or 1" or less is to feed raw plant material (or optionally rough chopped plant matter) into a shredder, granulator, a hammer mill, or a roller mill.

[0020] A granulator is a well-known machine designed for chopping or grinding material in various sizes. Most granulators contain multiple knives (often steel knives) and one or more screens (sometimes interchangeable) with various diameter holes to determine the size of the final product. Various granulators exist and may be useful in chopping the plant matter such as those containing openings of 3/8", 1/4" and 1/8".

[0021] As previously discussed, certain embodiments of the first embodiment and the processes of the second embodiment of the methods disclosed herein utilize a hammer mill. A hammer mill can generally be described as a steel drum containing a vertical or horizontal rotating shaft or drum on which hammers are mounted along with a surrounding screen-like material on the outer surface; the hammers "pound" the material that is passed through the mill. The hammers are generally flat metal bars often with some type of hardface treatment on the working ends. The hammers may be fixed or swinging. As the processed material passes through the screen openings, the size of the screen openings directly determines the final particle size of the hammer milled material.

[0022] Those embodiments of the first and second embodiments of the methods disclosed herein where a hammer mill is utilized, utilize a hammer mill having a screen with openings of less than 1/2" in size (i.e., a screen size of less than 1/2"). In certain embodiments, the screen of the hammer mill has openings of 7/16", 3/8", 5/16", 1/4", 3/16", 1/8" or 1/16". In other embodiments, the screen of the hammer mill has openings of 15/32", 7/16", 13/32", 3/8", 11/32", 5/16", 9/32", 1/4", 7/32", 3/16", 5/32", 1/8", 3/32", 1/16" or 1/32".

[0023] As previously discussed, certain embodiments according to the first and second embodiments disclosed herein utilize a roller mill. A roller mill/cracker mill can generally be described as a device with two or more rolls (configured in pairs) each containing longitudinal grooves which assist in further size reduction of material fed through the mill. Various size roller mills exist with the length and diameter of the rolls varying and the rolls also being available with various types of corrugation configurations. The corrugation configurations of the rolls are either referred to in terms of corrugations or grooves per inch (e.g., 6 grooves per inch, 8 grooves per inch) or by the opening size of the grooves (e.g., 3/4", 1/2", 3/8", 1/4" and 1/8"). Some rolls contain horizontal grooves (i.e., the grooves are parallel to the axis of rotation) and other rolls contain offset grooves (i.e., the grooves are offset from the axis of rotation by various degrees such as 5°). Furthermore, various profiles exist for the grooves, including round bottom vee (RBV), flat bottom vee, sawtooth with different leading and trailing angles, LePage cut with one roll corrugated longitudinally and one corrugated circumferentially, etc.. The size and profile of the grooves (i.e., the width and shape of the openings) determines the final size and shape of the roller milled material.

[0024] Those embodiments of the first and second embodiments of the methods disclosed herein where a roller mill is utilized, preferably utilize one pass through a roller mill set-up. In certain embodiments, the roller mill is configured with rolls that each have no more than 12 grooves per inch. Such a configuration may entail various set-ups including the use of two rolls each with 8 grooves per inch, two rolls each with 6 grooves per inch, one roll with 8 grooves per inch utilized with a second roll with 6 grooves per inch, two rolls each with 10 grooves per inch, two rolls each with 12 grooves per inch, one roll with 10 grooves per inch utilized with a second roll with 12 grooves per inch, etc. In other embodiments of the first and second embodiments of the methods disclosed herein, the roller mill is configured with rolls that each have no more than 8 grooves per inch. In certain of the foregoing embodiments of the first and second embodiments of the methods disclosed herein, the roller milling utilizes one pass through the rolls. In yet other embodiments of the first and second embodiments of the methods disclosed herein, the roller milling utilizes one pass through the rolls with a first roll having 6 grooves per inch and a second roll having 8 grooves per inch and the extractable rubber content is increased by at least 60%. The corrugations on each roll may be horizontal or offset. Various profiles may be used for the grooves on each roll, including, but not limited to RBV and straight profile.

[0025] In certain embodiments according to the first embodiment and processes according to the second embodiment disclosed herein, the plant matter that has been hammer milled and roller milled is also subjected to flake milling prior to processing for extraction of rubber. A flaker mill or flaker can generally be described as a device with two or more rolls each having a smooth surface, usually operated at different speeds, with a defined and adjustable clearance between rolls which primarily assist in providing further rupturing of plant cell walls. This type of mechanical treatment tends to increase the amount of natural rubber that can ultimately be recovered from the plant matter. In certain embodiments according to the first and second embodiments disclosed herein, the flake milling comprises one pass through a flaker. In other embodiments according to the first and second embodiments disclosed herein, the flake milling comprises multiple passes through a flaker, such as two passes, three passes or more. In those embodiments where at least one of roll milling, hammer milling, shredding, granulating or flake milling is used on the plant matter, the processed plant matter is preferably treated with at least one antioxidant if it will be stored prior to extraction of the rubber.

[0026] In certain embodiments according to the first and second embodiments of the methods disclosed herein, it can be helpful to treat the plant matter to remove undersize material at one or more stages. The plant matter may be treated to remove undersize material after chopping (i.e., prior to hammer milling or roller milling), after either hammer milling or roller milling or after each of hammer milling and roller milling. The amount of undersize material that is generated may vary depending upon various factors including the method that has been used to chop the plant material and the speed at which the chopping takes place. One exemplary way of removing undersize material is to pass the plant matter over a mesh screen that is then vibrated to allow undersize material to fall through the mesh. Various types of mesh screen may be utilized, depending upon the size of material that is classified as "undersize." In certain embodiments, a 30 mesh, 25 mesh, 20 mesh, 18 mesh or 16 mesh screen is utilized. The mesh rating of the screen corresponds to the number of openings per square inch. Hence a 20 mesh screen will have 20 openings in one square inch. The sizes of the openings in the listed mesh screens are as follows: 30 mesh (0.0232" openings or 595 micron openings); 25 mesh (0.0280" openings or 707 micron openings); 20 mesh (0.0331" openings or 841 micron openings); 18 mesh (0.0394" openings or 1000 micron openings); and 16 mesh (0.0469" openings or 1190 micron openings). Another exemplary way to remove undersize material is by using an air separator which functions to blow away or out undersize (and hence lighter) particles. Preferably when undersize material is removed (such as by a mesh screen), at least 90% by weight, even more preferably at least 95% by weight of the undersize material is removed. In certain embodiments according to the first and second embodiments disclosed herein, the plant material is processed prior to rubber extraction such that the plant material has a size of 1/16" to 1.5", preferably 1/16" to 1", even more preferably 1/8" to 1/2"; in certain such embodiments, the plant material has been subjected to a process such as granulation that utilizes a screen having openings of 1/16", 1/8", 1/4" or 1/2" thereby producing a material having a maximum size of no bigger than the openings.

Experiments:**Example 1**

5 **[0027]** A quantity of plant material was obtained from guayule shrubs that were almost 7 years old by harvesting the plants above the roots. Noticeably dead plants were not harvested, but some dead branches (estimated at about 5% by weight) were likely included. No operation was performed to remove leaves, but because of the time of harvest, spring regrowth of new leaves had not yet begun. Leaf weight (dry basis) was estimated to be less than 20%. The harvested plant matter was field dried for 10 days. Thereafter, the harvested plant matter was subjected to a coarse chopping process (using a chipper) to produce stick-like plant matter pieces with a diameter of 0.25" (0.64 cm) to 0.125" (0.31 cm) and an average length of about 1.75" (4.45 cm). Approximately two weeks thereafter, the chopped material was passed over a 20 mesh vibrating screen to remove undersize particles. About 7 weight % of the chopped material was -20 mesh. The plant material retained on the 20 mesh screen was then subjected to either hammer milling or roller milling in order to rupture the rubber-containing cells of the plant material. After hammer milling or roller milling, the plant material was again subjected to a 20 mesh (0.841 mm) vibrating screen to remove undersize particles. All -20 mesh materials were ultimately combined (regardless of equipment utilized) and a sample of the combined material was analyzed for moisture, rubber and resin content. In total, about 15 weight % of the original material was -20 mesh.

10 **[0028]** Two different screen sizes were evaluated for the hammer milling operation: 3/16" (0.5 cm) screen and 1/2" (1.2 cm). The hammer milling machine was a Roskamp Champion, 22" Challenger model (manufactured by CPM Roskamp Champion, Waterloo, Iowa) with a 30 horsepower motor and variable control settings for the hammer tip speed. The hammer mill was set at a tip speed to simulate a 44" hammer mill and operated at about 3600 rpm. The roller milling machine was a Roskamp Champion model TP 900-12 (manufactured by CPM Roskamp Champion, Waterloo, Iowa) equipped with three pairs of corrugated rolls (the rolls are each 9" in diameter and 12" in length). For the roller milling, two settings were evaluated. The first setting involved a one-time pass through a 6-8 corrugated roll set-up with two different rolls (one roll having 6 corrugations per inch and the second having 8 corrugations per inch). In this set-up, the first roll was corrugated with a 5° spiral curve and the second roll contained straight corrugations. The grooves of both rolls had a RBV profile (round bottom V shaped). The second setting involved a two-pass operation. The first pass was through a 10-12 corrugated roll set-up with two different rolls (one roll having 10 corrugations per inch and the other having 12 corrugations per inch, both having RBV grooves, one horizontal and the other 5° offset). The second pass was through the 6-8 corrugated roll set-up previously described.

15 **[0029]** Samples of the hammer milled and roller milled plant material were analyzed by hexane/acetone co-solvent extraction by the procedure in the next paragraph to determine the amounts of rubber and resin contained therein. Moisture content of the samples of plant material was determined by weighing samples of the plant material before and after drying at 110 °C in a forced-air oven for 5 hours. Results are reported in Table 1, below. Additionally, in order to determine the amount of rubber and resin lost as a result of using the 20 mesh vibrating screen, an adjusted calculation (using the amount of rubber and resin found in the combination of all -20 mesh material and the relative amounts lost during each milling operation) was made of the amounts of rubber, resin and moisture in the milled material product by each milling operation. Results of the adjusted calculations are reported in Table 2, below.

20 **[0030]** The plant material was then mixed (in a sealed 5-gallon plastic bucket) with a co-solvent mixture (containing 79:21 w/w of hexane:acetone). In each 5-gallon bucket, 5 pounds shrub material (2.27 kg), 12.6 pounds hexane (5.72 kg) and 3.4 pounds acetone (1.54 kg) were utilized. The mixtures were allowed to soak at room temperature occasional shaking for varying amounts of time from 24 hours to 2 weeks. After soaking, large shrub particles had gravity settled to the bottom of the bucket, allowing the top liquid phase to be decanted away. The top liquid phase was then subjected to two rounds of centrifuging. The centrifuge utilized was a bowl type with a swing-bucket rotor, operated at about 1000 rpm for about 45 minutes for each round. After each round of centrifuging, the clear supernatant was passed through a 45 micron screen. Additional acetone (in an amount of approximately 1:1, v/v of acetone:screened liquid) was then added to the screened liquid to cause the rubber to coagulate. The coagulated rubber was collected by decanting the liquid away. The rubber pieces were then redissolved in about 0.5 gallons of a mixture of hexane and acetone (79:21 w/w of hexane:acetone) and again coagulated by the addition of approximately 0.5 gallons more acetone. The coagulated rubber was again collected by decanting away the liquid and squeezing out excess solvent and then the rubber was vacuum oven dried about 15 hours at 65-70 °C. After drying, the rubber was weighed and re-dissolved with 1 phr antioxidant in hexane. After dissolving and mixing, the mixture was poured onto a large flat surface in the fume hood and the solvent was allowed to evaporate. After the initial drying, the rubber was weighed, then re-dissolved in a hexane solution containing 1 phr antioxidant (Santoflex® 134PD). After re-dissolving and mixing, the mixture was poured onto a large flat surface in the fume hood and the solvent was allowed to evaporate.

Table 1						
	Chopped plant material*	Hammer mill, 3/16" screen	Hammer mill, 1/2" screen	Roller mill 6-8 configuration	Roller mill 6-8 and 10-12 configuration	-20 mesh of all combined
Mean particle size (µm) ¹	1809	837	1230	--	1305	--
% moisture ²	15.45	14.96	15.31	14.44	14.84	14.13
% rubber ³	2.12	3.15	2.54	3.54	2.74	4.15
% resin ³	6.4	8.89	8.93	7.37	8.83	14.15
<p>1 Mean particle size was determined by sieve analysis.</p> <p>2 Percentage moisture was determined by weighing samples before and after drying for 5 hours at 110 °C in a forced air oven.</p> <p>3 Rubber and resin percentages reported are weight percentages of extractable rubber based upon the subjecting a sample of the respective plant material to a soxhlet-type extraction process with co-solvent of hexane and acetone (79:21, w/w hexane:acetone).</p>						

Table 2				
	Hammer Mill 3/16" Screens	Hammer Mill 1/2"Screens	Roller mill 6-8 configuration	Roller mill 10-12 and 6-8 configuration
% Moisture	14.88	15.19	14.42	14.77
% Rubber	3.25	2.70	3.57	2.87
% Resin	9.40	9.46	7.75	9.34

[0031] Samples of dried rubber obtained from guayule plant material that had been obtained as described above in paragraphs [00025]-[00028] were tested for molecular weight (using GPC, polystyrene standard) and for ash content (using thermogravimetric analysis "TGA"). The samples that were submitted for GPC and TGA analysis were taken from the vacuum dried rubber prior to re-dissolution and addition of antioxidant. (The rubber obtained from each of the roller milling and hammer milling treatments was combined together in no particular order, but, rather, as it was obtained such that there is no direct correspondence between Examples 1-5 of Table 3 and the examples that appear in Table 1.) For the TGA, a Q5000 model from TA Instruments was used with a standard heating protocol from room temperature to 550 °C and held for 4 hours. Results are reported in Table 3.

Table 3					
	#1	#2	#3	#4	#5
TGA residue, "ash" (weight %)	0.12	0.15	0.25	0.21	0.03
Molecular weight (x 10 ⁶)	1.21	1.36	1.48	1.33	1.40
Mw/Mn	3.36	3.51	4.10	3.92	3.99
Acetone extractables (weight %)	0.27	0.23	0.37	0.25	0.45

Example 2 - Hammer Milling, Roll Milling/Cracking and Flaking (Flake Milling)

[0032] Guayule shrub approximately 8-36 months old was harvested and bundled into bales. The bales were measured to have a moisture content of about 20-25%. Bales were fed to a standard wood chipper to reduce the guayule material

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into approximately 1" sticks. The shredded sticks of guayule were fed through a hammer mill by hand for further size reduction. The hammer mill then air conveyed the milled shrub through a fan to a cyclone separator. Varied screen sizes for the hammer mill (1", 1/2", 1/8", and 1/16") were used. The milled shrub was collected in bins and weighed as it was being produced.

5 **[0033]** All of the shrub was processed through a Sweco screener with a 20 mesh screen. The screener was used to remove fines from the shrub. It was tested before and/or after milling.

[0034] The milled shrub was processed in a cracker (also known as a roller mill), set up to have a differential roll speed of 1:1.1. The roll spacing on the cracker was adjustable. The cracker was fed using a vibratory screen feeder and the cracked material was collected in bins.

10 **[0035]** The cracked material was transferred to a flaker. The flaker had its own roll feeder, a differential roll speed of 1:1.25 and the roll spacing was set at 0.012". Samples of the flaked material were taken and retained for cell rupture analysis and for initial shrub rubber content. Some of the flaked material was retained to be run through the flaker a second and a third time. The flaked material was collected in bins and weighed. The final flaked material was refrigerated until it was ready to be extracted.

15 **[0036]** Determination of the % rubber and resin in samples was made using 9-10 gram samples of guayule material, soxhlet extracting for 6 hours with co-solvent (31 mL acetone, 170 mL pentane) to solubilize rubber and resin. Solubilized rubber (contained within the pentane phase) was isolated using methanol coagulation, centrifuging and drying. More specifically, 20 mL of the extract from the soxhlet extraction was transferred to a centrifuge tube and 20 mL of methanol was added to coagulate the rubber. The tube and its contents was centrifuged at 1500 rpm for 20 minutes to separate coagulated rubber from solvent. The supernatant within the tube was decanted into a flask and reserved for % resin determination. The tube and its coagulated rubber contents were rinsed with an aliquot of acetone (10 mL) and the acetone was poured out of the tube into the flask containing the decanted supernatant. The remaining coagulated rubber within the tube was then placed into a vacuum oven that had been pre heated to 60 °C and dried under vacuum for 30 minutes. After cooling to room temperature, the tube was weighed and the amount of rubber therein was calculated.

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25 Resin content (contained within the acetone phase) was determined by utilizing the flask containing the supernatant and decanted acetone. The solvent was evaporated from the flask in a fume hood until near dryness. The remaining contents were then further dried by placing the flask into an oven at 110 °C for 30 minutes. After cooling, the flask was weighed and the amount of resin remaining in the flask was calculated. Results are provided in Table 4 below.

Table 4

Conditions	Avg. %Moisture	Avg. % Rubber (Dry Weight Base)	Avg. % Resin (Dry Weight Base)
Shredded & Hammermilled 1/2"	26.79	2.34	6.70
Shredded & Hammermilled 1/8"	22.29	3.12	6.78
Shredded & Hammermilled 1/8" & 20 mesh screened & flaked	19.67	4.98	6.96
Shredded & Hammermilled 1/8" & 20 mesh screened & three passes flaked	19.52	5.61	7.33

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45 **[0037]** To the extent that the term "includes" or "including" is used in the specification or the claims, it is intended to be inclusive in a manner similar to the term "comprising" as that term is interpreted when employed as a transitional word in a claim. Furthermore, to the extent that the term "or" is employed (e.g., A or B) it is intended to mean "A or B or both." When the applicants intend to indicate "only A or B but not both" then the term "only A or B but not both" will be employed. Thus, use of the term "or" herein is the inclusive, and not the exclusive use. See Bryan A. Garner, A Dictionary of Modern Legal Usage 624 (2d. Ed. 1995). Also, to the extent that the terms "in" or "into" are used in the specification or the claims, it is intended to additionally mean "on" or "onto." Furthermore, to the extent the term "connect" is used in the specification or claims, it is intended to mean not only "directly connected to," but also "indirectly connected to" such as connected through another component or components.

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55 **[0038]** While the present application has been illustrated by the description of embodiments thereof, and while the embodiments have been described in considerable detail, it is not the intention of the applicants to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modifications will readily appear to those skilled in the art. Therefore, the application, in its broader aspects, is not limited to the specific details, the representative apparatus, and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the spirit or scope of the applicant's general inventive concept.

[0039] Aspects of the invention are set out in the following numbered clauses:

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1. A method for increasing the extractable rubber content of non-*Hevea* plant matter without unduly increasing the extractable resin content comprising:

utilizing a quantity of chopped non-*Hevea* plant matter having an average length of ½" to 4" and a maximum moisture content of about 15 weight % and subjecting the chopped non-*Hevea* plant matter to at least one of

hammer milling utilizing a screen size of less than ½"; and

roller milling with corrugated rolls having no more than 12 corrugations per inch,

thereby producing a quantity of milled non-*Hevea* plant matter having a maximum moisture content of about 15 weight %, an extractable rubber content at least 30% higher than the pre-milled chopped non-*Hevea* plant matter.

2. A method according to clause 1, wherein the non-*Hevea* plant matter is from guayule shrubs.

3. A method for increasing the extractable rubber content of guayule shrub plant matter without unduly increasing the extractable resin content comprising:

utilizing a quantity of chopped guayule shrub having an average length of ½" to 4" and a maximum moisture content of about 15 weight % and subjecting the chopped guayule shrub plant matter to

hammer milling utilizing a screen size of less than ½";

optionally roller milling with corrugated rolls having no more than 12 grooves per inch, and

flake milling,

thereby producing a quantity of milled guayule shrub plant matter having a maximum moisture content of about 15 weight %, and an extractable rubber content at least 100% higher than the pre-milled chopped guayule shrub plant matter.

4. A method according to any one of clauses 1-3, wherein the milled non-*Hevea* plant matter has an extractable resin content of no more than 3 times the extractable rubber content.

5. A method according to any one of clauses 1-3, wherein the hammer milling utilizes a screen size of 3/16" or smaller.

6. A method according to any one of clauses 1-3, wherein the hammer milling utilizes a screen size of 3/16".

7. A method according to any one of clauses 1-3, wherein the roller milling utilizes corrugated rolls having no more than 8 grooves per inch.

8. A method according to any one of clauses 1-3, wherein the roller milling utilizes one pass through the rolls.

9. A method according to any one of clauses 1-3, wherein the roller milling utilizes one pass through the rolls with a first roll having 6 grooves per inch and a second roll having 8 grooves per inch and the extractable rubber content is increased by at least 60%.

10. A method according to any one of clauses 1-3, wherein the chopped non-*Hevea* plant matter has an average length of less than 2" and contains no more than 1 weight % of material with a mesh size less than 20.

11. A method according to any one of clauses 1-3, wherein the milled non-*Hevea* plant matter is subjected to a particle size screening to remove at least 90 weight % of the particles having a size of less than 20 mesh prior to subjecting to a water-based or organic solvent based rubber extraction process.

12. A method according to clause 1 or 2, further comprising flake milling the milled non-*Hevea* plant matter.

13. A method according to any one of clauses 1-3, further comprising subjecting the milled non-*Hevea* plant matter

to a screening process to remove undersize plant matter.

14. A method according to clause 13, wherein the undersize plant matter is less than 20 mesh.

5 15. A method according to clause 3, wherein the flake milling comprises multiple passes through a flaker.

16. A method according to clause 3, wherein the roller milling is not optional.

10 **Claims**

1. A method for increasing the extractable rubber content of guayule plant matter comprising:

15 utilizing a quantity of chopped guayule plant matter having an average length of ½" to 4" and a maximum moisture content of 15 weight % and subjecting the chopped guayule plant matter to hammer milling utilizing a screen size of less than ½", thereby producing a quantity of milled guayule plant matter having a maximum moisture content of 15 weight % and an extractable rubber content at least 30% higher than the pre-milled chopped guayule plant matter.

20 2. The method of claim 1, wherein the milled guayule plant matter has an extractable rubber content at least 40% higher than the pre-milled chopped guayule plant matter

3. The method of claim 1, wherein the milled guayule plant matter has an extractable rubber content of from at least 30% higher up to 60% higher than the pre-milled chopped guayule plant matter.

25 4. The method of any one of claims 1-3, wherein the milled guayule plant matter has an extractable resin content of no more than 3 times the extractable resin content of the pre-milled chopped guayule plant matter.

30 5. The method of any one of claims 1-3, wherein the milled guayule plant matter has an extractable resin content of no more than 2 times the extractable resin content of the pre-milled chopped guayule plant matter.

6. The method of any one of claims 1-3, wherein the milled guayule plant matter has an extractable resin content of no more than 1.5 times the extractable resin content of the pre-milled chopped guayule plant matter.

35 7. The method of any one of claims 1-6, wherein the hammer milling utilizes a screen size of less than ½", but greater than or equal to 1/16".

8. The method of any one of claims 1-6, wherein the hammer milling utilizes a screen size of 3/16" to 1/16".

40 9. The method of any one of claims 1-6, wherein the hammer milling utilizes a screen size of 7/16".

10. The method of any one of claims 1-6, wherein the hammer milling utilizes a screen size of 3/8".

45 11. The method of any one of claims 1-6, wherein the hammer milling utilizes a screen size of 5/16".

12. The method of any one of claims 1-6, wherein the hammer milling utilizes a screen size of 1/4".

50 13. The method of any one of claims 1-12, wherein the milled guayule plant matter is subjected to a particle size screening to remove at least 90 weight % of the particles having a size of less than 20 mesh prior to subjecting to a water-based or organic solvent based rubber extraction process. [

14. The method of any one of claims 1-12, further comprising subjecting the chopped guayule plant matter to a screening process to remove undersize plant matter of less than 20 mesh.

55 15. The method of any one of claims 1-14, further comprising flake milling the milled guayule plant matter.



EUROPEAN SEARCH REPORT

Application Number
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Place of search Munich		Date of completion of the search 4 May 2017	Examiner Barker, Stephan
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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ANNEX TO THE EUROPEAN SEARCH REPORT
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